# ISOTOPIC STUDY OF AN EASTERN OHIO CARBONATE CONCRETION

BY

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ABSTRACT

The isotopic composition of a Pennsylvanian siderite concretion indicates that the concretion is of marine origin. The $\delta^{13}C$ of the siderite was +.7 or .6, essentially equal to the marine carbonate used as standard. The $^{87}Sr/^{86}Sr$ ratio of the siderite was slightly higher than the accepted value for Pennsylvanian seawater. This can be attributed to the insoluble silica residue in the siderite, incomplete mixing with worldwide ocean water or the particular sample area was not exactly representative of the entire depositional basin. At least some of the sulfur is secondary with the sulfate $\delta^{34}S$ value (4.6) being too low for deposition from Pennsylvanian seawater. The sulfides present ($FeS_2$ and ZnS) did not precipitate from the same solution. Pyrite was probably reduced from the seawater, with $^{32}S$ being biologically enriched. The sulfate that is in the sample is of non-marine origin and was most likely oxidized from the sphalerite since both have the same $\delta^{34}S$ of -4.6. A source of this sulfur is either old sulfide (probably pyrite) or of magmatic origin.

## Introduction

Coals from eastern Ohio and other Applachian coal belt areas are hampered in the market because of a high sulfur content. With the ever increasing importance of coal in meeting the U.S.'s energy demands, information regarding this sulfur to determine its extent, variation of concentrations, and mineral form in the coal producing regions is needed. This information could lead to the avoidance of as much sulfur as possible in coal recovery and to the possible discovery of economically important ore deposits of sulfides (zinc, or copper, or lead, or nickel). The objectives of this study are to learn the sources of this sulfur and how it came to be deposited in the coal and associated shale beds. Studying the source and mode of deposition of the carbon in the carbonate concretion which contained the sulfur will help to discover the relationship between the sulfur and the coal horizon.

Analysed was a carbonate concretion, (clay ironstone), sample 1229, approximatly 12"-7"-5". It was broken into five fragments which shall be refered to as fragments A through E. Barite and sphalerite were indistinguisable from calcite and galena respectively until they were identified by X-Ray Diffraction.

Fragment A (approx. 8"-6"-4") Slightly purplish dark gray carbonate surrounded by a dirty gray carbonate ring. Cavity and fracture veins contain white to very light gray barite, some showing good

clevage. Crystals in cavity tend to grown radiating from a point. Some copper staining towards center of cavity. Kaolinite and limonite occuring in cavity. Some bright green copper, dark green and purplish black copper stained drusy pyrite clumps around inside of cavity. Intergrown with some of the barite are a few small black tabular crystals of sphalerite. Cavity is ring-like, with some limonite stained carbonate protruding in center.

Fragment B (approx size - 6" - 4" - 3") Conchoidally fractured dark gray carbonate with veins and thin cavities of white, light brownish pink and gray barite. The barite shows good clevage. Veins also of well formed pyrite with some veins having pyrite from one direction and barite from the other. Small flecks of pyrite occuring throughout barite crystals, with some drusy formed pyrite on the barite. Fracture veins are 1/16" to 1/8" wide. Vugs of barite grown radiating from a point.

Fragment C (approx. size 5" - 3½" - 2") Conchoidally fractured dirty gray carbonate with darker outer rim. Fracture veins containing pyrite connected with veins and small cavites filled with white, tan, and bluish gray vitreous barite.

Fragment D (approx. size 4" - 2" - 1½") Same as Fragment C except larger cavity of pyrite and barite not as vitreous.

Fragment E (approx size 2" - 1" - ½") Dirty gray carbonate with fractures filled with pyrite and small fractures filled with white barite.

The specimen was obtained from a shale bed between the No. 5 and No. 5A coal seams in north-central Tuscarawas county. The concretion was found in an operating coal mine. name ?

Fragment A of 1229

Gray Areas- Siderite

Lightest Areas- Barite

Darkest Areas- Sphalerite

Fragment B of 1229

Darkest Areas - Pyrite
Lightest Areas - Barite
Gray Areas - Siderite

General Geology of Area

The Pennsylvanian system contains the chief coal producing series in the eastern United States. The rocks of this system outcrop along the Appalachian Basin from Pennsylvania, southwest to northern Alabama and include eastern Ohio, West Virginia, western Maryland, central Tennessee. In the Appalachian Basin this system is made up of mostly sandstone and shale, interbedded with comparatively thin but frequently recurring beds of coal, clay, limestone, and iron ore. Known chiefly for its mineable coal beds; the clays, shales, sandstones, and iron ores have had economic importance.

In Ohio the Pennsylvanian outcrops over an area of 10,464 sq. miles. The total thickness of the system in Ohio averages 1,100 feet. Forty-four separate and distinct coal beds and twenty-seven separate and distinct limestone horizons of Pennsylvania time in the state illustrate the cyclic nature of sea advance and retreat of this time. The coal beds and their underclays are separated in vertical section by sandstone and shale beds, with minor amounts of limestone and iron ore.

The Pennsylvania is divided into four subdivisions, which are from bottom to top, the Pottsville, Allegheny, Conemaugh, and Monongahela series. Of these the upper half of the Pottsville series, the Allegheny series, and the lower three-fourths of the Conemaugh series outcrop in Tuscarawas County. All bedrock that is exposed in the county is Pennsylvanian in age. The siderite concretion sample (1229) was recovered from the middle of the Allegheny series.

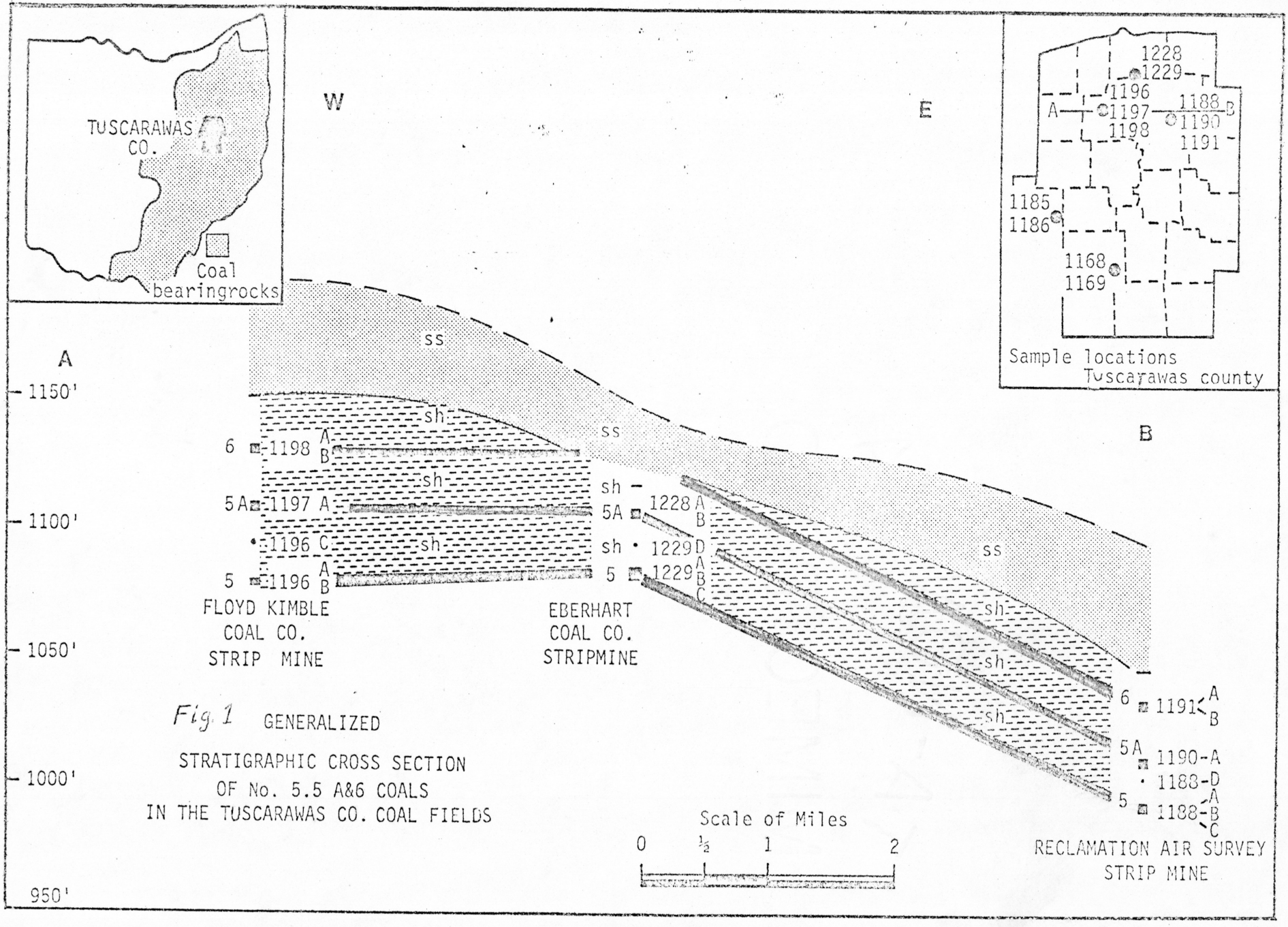



*Fig. 1* GENERALIZED

STRATIGRAPHIC CROSS SECTION
OF No. 5.5 A&6 COALS
IN THE TUSCARAWAS CO. COAL FIELDS

Procedure for Analysis

The minerals were separated by hand picking. This could be done because most of the different minerals were well separated. Pyrite and barite were collected from the veins and cavities of two of the fragments. A small amount of sphalerite was recovered from fragment A and some of the clay ironstone (siderite) was sampled from all of the fragments. All of the minerals were then ground to 200 mesh.

MINERAL IDENTIFICATION (By X-Ray Diffraction)

Some of the mineral powder is spread uniformly over a glass slide, using a small amount of adhesive binder. There will be thousands of tiny crystalline particles on the slide in random orientation that reflect x-rays.

The slide is clamped in place and rotates about a stream of monochromatic x-rays, while an x-ray detector, mounted on an arm, rotates about it to pick up the diffracted x-ray signals.

At the zero setting the x-ray beam is parallel to the slide and passes directly into the x-ray detector. A motor drives the slide and detector with the detector rotating $2\theta$ for every $\theta$ the slide rotates. Set in motion simultaneously with the sample (slide) and the x-ray detector, is the paper drive of the strip chart. The chart moves at a constant speed corresponding to the rate of rotation of the slide. If an atomic plane has interplanar spacing such that a reflection occurs at $\theta = 15^{o}$, then when the counting tube has been rotated to $2\theta$, or $30^{o}$, the diffracted beam enters the x-ray

Correlation Between 2θ Expected Peaks And 2θ Observed Peaks. (From X-Ray Diffraction Charts)

XRD Using: Cu K-alpha radiation
Ni filtered, 45 kilovolt
15 milliamps
Xe-filled Geiger tube

| 1229 B Pyrite $FeS_2$ | 2θ Expected | 2θ Observed |
|---|---|---|
| | 56.34 | 56.4 |
| | 33.07 | 33.0 |
| | 37.10 | 37.2 |
| | 40.79 | 40.8 |
| | 47.75 | ..... |
| | 28.54 | 28.5 |

| 1229 D Pyrite $FeS_2$ | 2θ Expected | 2θ Observed |
|---|---|---|
| | 56.34 | 56.4 |
| | 33.07 | 33.1 |
| | 37.10 | 37.2 |
| | 40.79 | ..... |
| | 47.75 | 47.6 |
| | 28.54 | 28.6 |

| 1229 A Sphalerite $ZnS$ | 2θ Expected | 2θ Observed |
|---|---|---|
| | 28.58 | 28.6 |
| | 47.56 | 47.5 |
| | 56.34 | 56.4 |
| | 33.12 | 33.1 |

| 1229 A Barite $BaSO_4$ | 2θ Expected | 2θ Observed |
|---|---|---|
| | 25.88 | 26.0 |
| | 28.79 | 28.9 |
| | 42.65 | 42.8 |
| | 42.99 | 43.0 |
| | 26.88 | 26.9 |
| | 22.80 | 22.9 |
| | 31.57 | 31.7 |
| | 32.85 | 32.9 |

| 1229 B Barite $BaSO_4$ | 2θ Expected | 2θ Observed |
|---|---|---|
| | 25.88 | 26.0 |
| | 28.79 | 28.9 |
| | 42.65 | 42.8 |
| | 42.99 | 43.0 |
| | 26.88 | 27.0 |
| | 22.80 | 22.9 |
| | 31.57 | 31.7 |
| | 32.85 | 32.9 |

| 1229 Siderite $FeCO_3$ | 2θ Expected | 2θ Observed |
|---|---|---|
| | 32.09 | 32.0 |
| | 52.92 | 52.9 |
| | 52.76 | 52.7 |
| | 46.27 | 46.2 |
| | 24.80 | 24.8 |
| | 42.42 | 42.4 |
| | 38.45 | 38.5 |

Insoluble Residue of Siderite, 1229

| Quartz | 2θ Expected | 2θ Observed |
|---|---|---|
| | 26.66 | 26.7 |
| | 20.85 | 20.9 |
| Kaolinite | 12.34 | 12.4 |
| | 24.88 | 24.9 |

There also was a broad peak at 24.9 that might be of organic origin. A small Illite peak at 8.9 also appeared. ✓

detector. This causes a response from the detector which is amplified and causes a deflection on the recording strip chart. The angle 2θ can be read from the chart as a peak, with the peaks directly proportional to the intensities of the diffraction effects. The peaks are then compared to tables that contain all the various mineral listings.

## ISOTOPIC MEASUREMENTS OF SULFUR AND CARBON

Sulfur has four stable isotopes ($^{32}S$, $^{33}S$, $^{34}S$, and $^{36}S$) which vary in nature by physicochemical and biologic processes. The most significant of these is due to the fractionation associated with bacterial (Desulfovibrio) reduction of sulfate to sulfide ions. Baterial reduction increases the abundance of $^{32}S$ in the sulfide and leaves the residual sulfate enriched in the heavier isotopes. The isotopic composition of a sulfur sample is expressed as:

$$\delta^{34}S = \frac{(^{34}S/^{32}S)_{spl} - (^{34}S/^{32}S)_{std}}{(^{34}S/^{32}S)_{std}} \times 10^3 \text{ o/oo}$$

where $(^{34}S/^{32}S)$ spl is the ratio of these isotopes in the sample and $(^{34}S/^{32}S)$ std is the ratio in troilite (FeS) of the iron meteorite Canyon Diablo. A positive value of $^{34}S$ means enrichment in $^{34}S$ relative to standard; a negative value indicates enrichment in $^{32}S$.

Carbon's isotopes ($^{12}C$ and $^{13}C$) are also fractionated by natural processes. Photosynthesis leads to enrichment of $^{12}C$ in carbon compounds of biologic origin. Isotope exchange reactions between $CO_2$ gas and aqueous carbonates

species enrich carbonates with $^{13}C$. The isotopic composition of carbon is expressed in the same manner as sulfur's and is defined by the equation:

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{spl} - (^{13}C/^{12}C)_{std}}{(^{13}C/^{12}C)_{std}} \times 10^3$$

The standard is taken from the isotopic composition of the carbon of belemnites of the Peedee formation (PDB).

Both the isotopic analyses of sulfur and carbon were done by Geochron Laboratories in Cambridge. Mass.

## ISOTOPIC MEASUREMENT OF STRONTIUM

Some finely powdered siderite was pressed into a tablet. This was then subjected to X-ray fluorescence to determine the concentration of strontium in sample (see table on the following page).

Siderite powder was dissolved in HCl. This was filtered and the insoluble residue was analysed by x-ray diffraction and determined to be quartz, kaolinite, and some mixed layered clays.

The filtrate was then placed in a cation exchange column where it was collected in fractions by the sequential running thru of HCl. The most radioactive fractions were then used to coat a filament on the mass spectrometer which was heated to volatilize the strontium.

These ~~molecules~~ atoms of strontium are ionized ~~by bombardment with electrons.~~

X-ray fluorescence using a Mo-target x-ray tube, LiF(220) diffracting crystal, and a scintillation detector. Tube operated at 65 kVP and 55 ma.

| Sample | Time | (30.00) MoKαC x100 | (35.20) B1 x100 | (35.85) Sr x200 | (36.50) B2 x100 | Elapsed Time | Net Sr | Net Sr / MoKαC | f | (Sr/MoKαC)c | Sr | Avg. Sr PPM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 48R4 | 2:08 | 24920 | 3781 | 14733 | 3440 | 0 | 7512 | .30144 | —— | —— | —— | |
| 1229 | 2:21 | 11156 | 2089 | 9042 | 1891 | 13 | 5062 | .45375 | 1.04738 | .47524 | 290.24 | |
| 1229 | 2:36 | 11373 | 2107 | 9135 | 1924 | 28 | 5104 | .44878 | 1.05017 | .47129 | 287.83 | 289.04 ✓ |
| 48R4 | 2:49 | 25527 | 3821 | 14915 | 3454 | 41 | 7640 | .29929 | —— | —— | —— | |

Calibration:

48R4 : $\frac{Sr\ net}{MoK\alpha C} = 0.3150$

$Sr = 610.568 \left(\frac{Sr\ net}{MoK\alpha C}\right) + 0.07759$ ppm

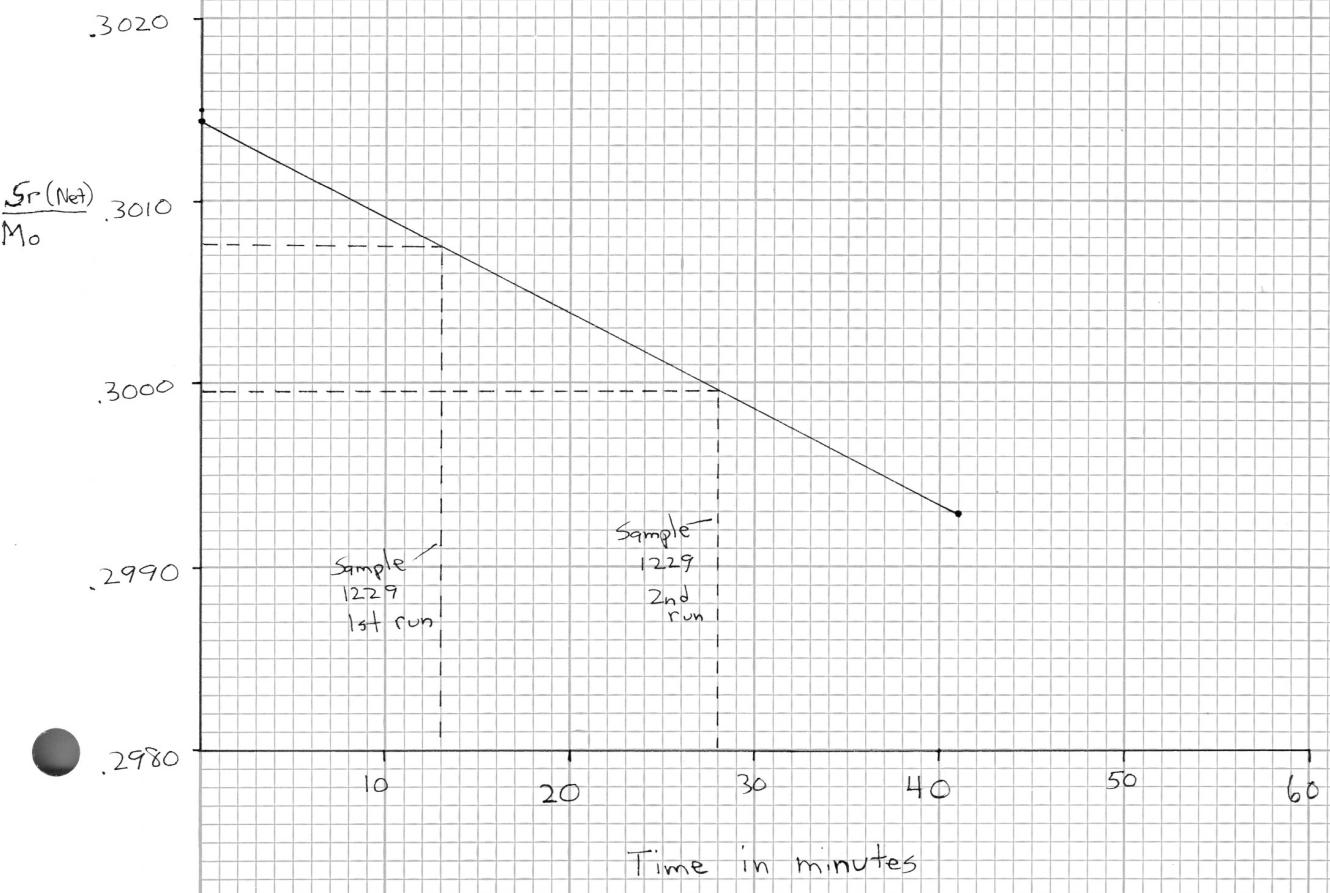
[Based on calibrations using rock standards of the U.S. Geol. Survey (G-2, GSP-1, BCR-1, AGU-1, W-1)]

Notes: $MoK\alpha C = Mo\text{-}k\text{-}\alpha$ compton scattered

$Net\ Sr = Sr(35.85) - \frac{(B1 + B2)}{2}2 = Sr(35.85) - B1 - B2$

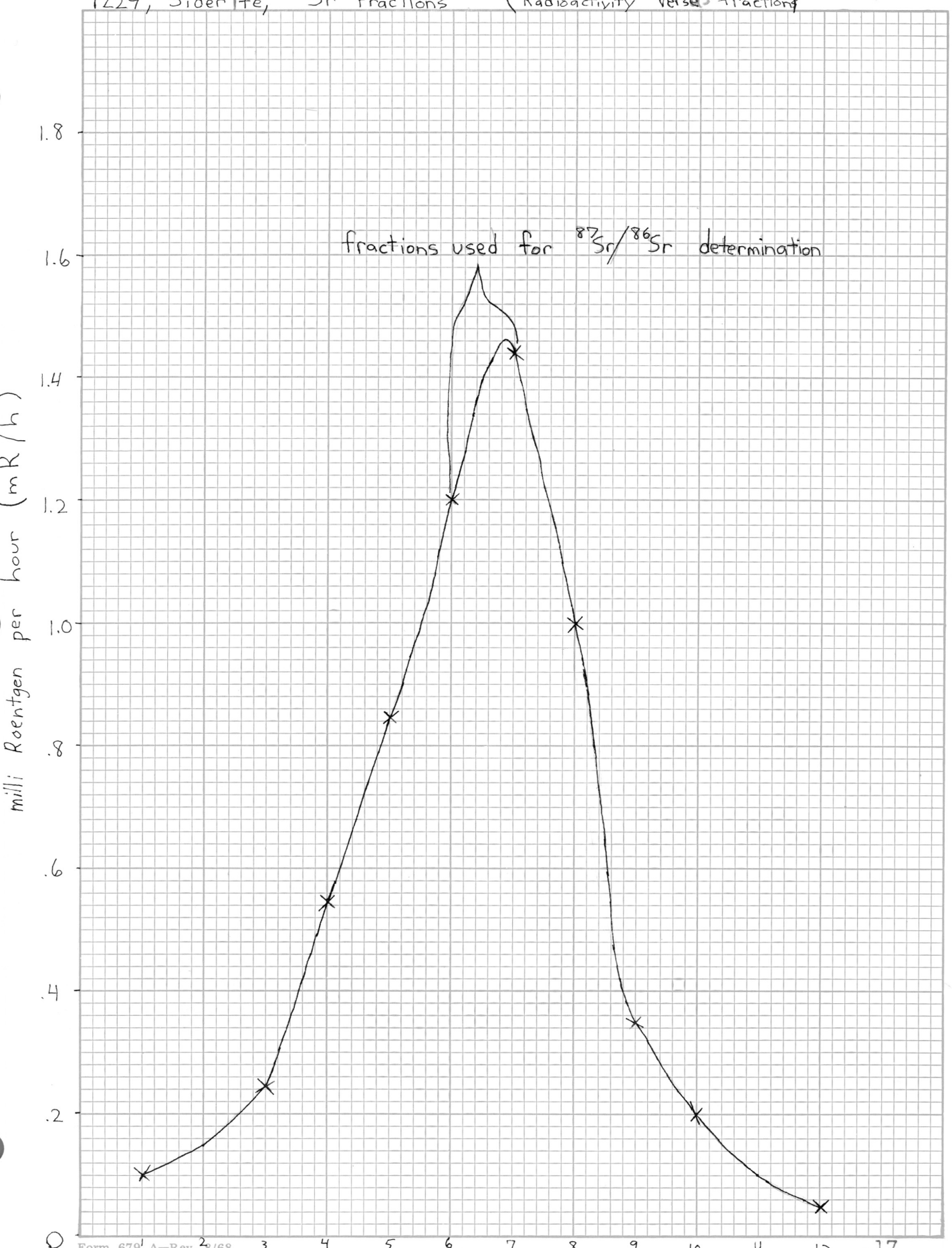
$\left(\frac{Sr}{MoK\alpha C}\right)_c = \frac{Net\ Sr}{MoK\alpha C} \times f$

Graph For Calibration for machine drift dependent on time, during X-ray fluorescence.




$$f = \frac{0.3150}{\text{interpolated value of } \frac{Sr(Net)}{Mo}}$$

1229, Siderite, Sr Fractions (Radioactivity verses fractions)



This ion beam enters a magnetic field that deflects the ions. The heavier the ion the ~~more~~ less the deflection. The separated ion beams move to the ion collector which is a metallic cup behind a slit plate. One beam at a time enters the collector and is neutralized by electrons that flow from ground to the collector through a resistor. The voltage difference across the resistor is measured and recorded on a strip chart. By focusing the different beams into the collector one gets the peaks and valleys that form a mass spectrum for each element. Each peak represents an isotope with the peak's height proportional to the abundance of that isotope.

# $^{87}Sr / ^{86}Sr$ Determination for Siderite, 1229

$$\frac{87}{86} = 0.71096 \pm 0.00190 \quad (1\sigma)$$

$$\frac{86}{88} = 0.119420 \pm 0.00037 \quad (1\sigma)$$

$$\left(\frac{87}{86}\right)_c = 0.71101 \pm 0.00113 \quad (1\bar{\sigma})$$

Best Value:

$$0.71101 \pm 0.00043 \quad (1\sigma)$$

$$1\sigma = \sqrt{\frac{\Sigma (x-\bar{x})^2}{n-1}} \quad \text{(standard deviation)}$$

$$1\bar{\sigma} = \sqrt{\frac{\Sigma (x-\bar{x})^2}{n(n-1)}} = \frac{\sigma}{n} \quad \text{(standard deviation of the mean)}$$

## Results and Discussion

Where is the Table of $\delta^{34}S$ ?

### SULFUR ANALYSIS

Sulfur is found in coal as (1) sulfides (usually $FeS_2$); (2) sulfates of Ca, Sr, Ba, or Fe; (3) sulfur atoms bonded to the carbon, hydrogen or nitrogen of the coal. Of these, occurrences as sulfides are the most important in both coal and associated sedimentary rocks.

When sulfides are cogentic and precipitated from aqueous solution or crystallized from sulfide liquids, the $^{34}S$ values will be slightly different and vary according to the mineral's bond strength. So assuming the sulfides are from the same source and formed at equilibrium then an isotopic equilibrium temperature can be obtained by using the equation:

$$\Delta^{34}S = \frac{A \times 10^6}{T^2}$$

Using an A value of 0.356, reported by Sakai (1968), and $\Delta^{34}S = \delta^{34}S_{\text{pyrite}} - \delta^{34}S_{\text{sphalerite}} = 6.2$ colloquial you end up with a temperature of 240 K or -33 C.

This unreasonable result means that, since Sakai's report has not been invalidated, the sulfur came from different sources or was not deposited under equilibrium conditions. ✓

Because of the large difference in the sulfides $\delta^{34}S$ and since they are not intergrown in the concretion they seem to have been deposited at different times. Also it is typical for pyrite to have a higher $\delta^{34}S$ value than sphalerite when deposited together.

Seawater contains large amounts of sulfur in the form of sulfate ions in solution. This has caused marine sulfur $\delta^{34}S$ to vary from +10 to +30 ~~ppm.~~ o/oo. Pennsylvanian sulfur was close to +13 ppm. Reduction of this sulfate by bacteria could have been sufficient to enrich the resulting sulfide in $^{32}S$ to the value of the pyrite ($\delta^{34}S$= -10.8 ). The barite in the sample would have a positive ( > 12) $^{34}S$ if deposited at this time. Since the sulfate ($BaSO_4$) has a negative $\delta^{34}S$ value, its source must have been negative since bacterial action would increase the $\delta^{34}S$ of a sulfate residue. Oxidation of sulfur an old pyrite source (one that was enriched in $^{32}S$ )relative to marine sulfur) or a magmatic sulfur source would be needed to produce the sulfate at -4.6. Since it's $\delta^{34}S$ value is also -4.6 the sphalerite would have come from the same source.

## CARBON ANALYSIS

There are three different possibilites for the origin of the carbon: (1) $CO_2$ by oxidation of the coal; (2) precipitation of marine carbonates from bicarbonates; (3) precipitation of non-marine carbonates from bicarbonates. These processes yield markedly different $^{13}C$ values.

Biogenic carbon has been strongly enriched in $^{12}C$ thru photosynthesis ( $\delta^{13}C$ from -24 to -34 ppm for land plants, -6 to -19 ppm for aquatic and marsh plants). No change occurs in coalification while in maturation of liquid and gaseous hydrocarbons further enrichment of $^{12}C$ occurs. In equilibrium carbonate precipitation the $\delta^{13}C$ value is increased by about 10 ppm from that of the $CO_2$ gas. This leaves marine carbonates with a $\delta^{13}C$ value of $0.56 \pm 1.55$ and freshwater carbonates a $\delta^{13}C$ of $-4.93 \pm 2.75$. The enrichment in $^{12}C$ and greater variability of freshwater is thought to be caused by $CO_2$ from oxidation of biologic material in soils. Marine carbonates would be expected to be nearly zero since the standard is of marine origin. The siderite's carbon was determined to be $\delta^{13}C = .7$ or .6 . Both figures would clearly show the carbon to be of marine origin.

## STRONTIUM ANALYSIS

It is thought that the isotopic composition of the oceans is homogeneous and varies with time according to the mixing ratios of: (1) young volcanic rocks with an average $^{87}Sr/^{86}Sr$ of 0.704 $\pm$ 0.002; (2) old sialic rocks of continental crust that average 0.720 $\pm$ 0.005; and (3) marine carbonates of Phanerozoic age averaging 0.708 $\pm$ 0.001. Since seawater $^{87}Sr/^{86}Sr$ ratios have changed relatively little, marine carbonates fall into a narrow range of $^{87}Sr/^{86}Sr$ ratios. Non-marine carbonates can receive their strontium from selective sources so their $^{87}Sr/^{86}Sr$ ratios cover a much wider range and are dependent on their sediment's provenances.

The $^{87}Sr/^{86}Sr$ ratio for the siderite in the sample was 0.7110 with 290 ppm of strontium present. This is slightly higher than the 0.7085- 0.7090 $^{87}Sr/^{86}Sr$ ratio reported by Peterman,Doe, and Prostka in 1970 for marine carbonates of Pennsylvanian age. Since the margin of disagreement with Pennsylvanian seawater is small then it is possible that the siderite is of marine origin but since the sorrounding area lacked volcanic activity and the sediment sources were of older rocks then the shallow Pennsylvanian sea was slighty enriched in $^{87}Sr$. Poor drainage, which would be associated with a swampy coal producing area, might

help in localizing this sediment with a higher $^{87}Sr/^{86}Sr$ ratio. Rubidium could have traveled via silicate grains into the sediment and then decayed into radiogenic $^{87}Sr$, increasing the $^{87}Sr/^{86}Sr$ ratio. Quartz was identified as one of the major insoulbe residue components in the siderite. What drainage did come into the area was most likely from the east or northeast where older rocks were being eroded. If the siderite is non-marine then it would have become enriched in $^{87}Sr$ the same way and simply have had no interaction with Pennsylvanian seawater.

## SUMMARY

The most feasible source for the large amounts of sulfur that reside in Pennsylvanian rocks, both coal and shale beds, is the Pennsylvanian sea. This seawater repeatedly covered the Appalachian coal swamps of the time. Although the barite and the sphalerite formed from a non-marine source the pyrite was of marine origin, and pyrite is the most important from of sulfur in Ohio coal beds. Coal from freshwater basins would therefore have less sulfur than the large coastal plain deposits.

The carbon isotopic ratio strongly suggests a marine enviroment, the Pennsylvanian sea, for deposition of the siderite concretion. This agrees with the concept of repeated indunation of the coal swamps by the advancing sea and deposition of shale over the peat.

Since the sample represents only one discrete area of deposition and not the entire depositional basin it can be conceived as marine even though it's $^{87}Sr/^{86}Sr$ ratio is slightly higher than the seawater of that time period. Further sampling and $^{87}Sr/^{86}Sr$ ratio determination would confirm or refute this.

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